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N. Kristianpoller+ and R. A. Knapp
Institute of Optics
University of Rochester
Rochester 27, New York

+ On leave from the Department of Physics, Hebrew University, Jerusalem, Israel.

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Some Optical Properties of Sodium Salicylate Films*

N. Kristianpoller+ and R. A. Knapp

Institute of Optics, University of Rochester

Rochester 27, New York

Abstract

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Measurements of emission and absorption spectra and relative quantum yield of luminescence of sodium salicylate have been carried out in the wavelength range between 1750 and 5000Å at room temperature and at 80°K for different thickness samples. Among effects noted are an increase in total emission intensity of approximately 25% on cooling, a rather deep absorption hole at 2700Å and pronounced decreases in the relative quantum yield at 2700Å and at 2000Å.

* Research supported by the National Aeronautics and Space Administration, Goddard Space Flight Center.

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INTRODUCTION

It has previously been reported that the luminescent efficiency of sodium salicylate is independent of the intensity of the exciting radiation and that the relative quantum yield of the material is constant over a wide spectral range [1-4]. Because of these properties the phosphor has become a widely used wavelength conversion detector for the ultraviolet. While using sodium salicylate in our laboratory, however, it became apparent that under certain conditions the quantum yield was not as constant as had been assumed. The experiments described in the following were therefore undertaken in order to determine the magnitude and possible causes of these departures from the condition of constant quantum yield.

EXPERIMENTAL

Polycrystalline layers of sodium salicylate of different thicknesses were used as samples for our experiments. These layers were prepared by either sedimentation or by spraying on glass or quartz substrates. A spray method developed by one of us (RAK), see Appendix, was found to be the most convenient and useful for preparing fine grained and uniform layers.

For emission spectrum measurements the sample was illuminated by the 2537Å Hg line, isolated by a B&L grating monochromator, and the luminescence was analyzed with a

Leiss single prism monochromator. In order to determine the temperature dependence of the emission the sample was mounted in a vacuum cryostat which was provided with fused silica windows.

Absorption spectra were taken in the range 2000-5000Å with a Cary recording spectrophotometer (Model 14). Appropriate filters were used to determine the level of possible sample luminescence in the transmitted light.

At wavelengths longer than 2000Å excitation spectra were measured relative to a thermocouple using a previously described method[5]. Figure 1a shows the schematic arrangement. Most of these measurements were made with the exciting radiation normally incident on the sample and the luminescence passing through the phosphor and substrate to the photomultiplier. This is the method illustrated in Figure 1a and is referred to as the forward position of measurement or "position A". Some measurements were also made by observing the luminescence emerging from the irradiated side of the phosphor; this method is referred to as the backward direction of measurement or "position B". Suitable filters were used in front of the photomultiplier to exclude any of the exciting radiation and to determine the level of scattered light from the source. Samples used for these measurements ranged in thickness from 0.2 to 10.0 mg/cm^2.

For measurements of the excitation spectrum in the

region 1750 to 2200Å the apparatus shown schematically in Figure 1b was used. Complete descriptions of the monochromator and associated equipment are found elsewhere[6,7]. Here the samples of sodium salicylate were deposited on the face of the light pipe which transmitted the luminescence to the external photomultiplier. In order to exclude shorter wavelength radiation and to decrease stray light response a special chopper was fabricated using alternate sections of fused silica, absorption edge approximately 1600Å, and Vycor, absorption edge approximately 2200Å.

RESULTS AND DISCUSSION

Emission spectra of a sodium salicylate sample are shown in Figure 2. Curve 2a shows the spectrum at room temperature while curve 2b was taken at 80°K. A very slight shift of the maximum to shorter wavelength may be seen in the latter curve as well as an increase in total emission intensity of approximately 25%.

Results of excitation spectra measurements for three samples at room temperature are shown in Figure 3. The ordinate η is the relative quantum yield per incident photon;

$$\eta = k \frac{I}{\lambda V}$$

where I is the photomultiplier anode current, V is the EMF of the thermocouple and k is an instrumental constant. The

thinnest sample, #3, shows a lower yield and a significant drop at 2700Å and all samples exhibit a noticable decrease between 2200 and 2000Å.

In his work on sodium salicylate Hamann[4] noticed a slight increase in the relative yield of the phosphor near 2700Å for thick layers, $t > 1.6$ mg/cm^2, when observed in the forward direction but no change in the yield in the backward direction and no change in either direction for thin layers. It was suggested that the increase near 2700Å was due to a lower reabsorption by the phosphor but the author agreed that this explanation could not account for the observed flatness of the yield curves for thinner samples or for thicker samples in the backward direction of observation. A more reasonable explanation for the behavior observed here is seen in Figure 4 which shows the absorption spectrum of a thin, $t \simeq 0.2$ mg/cm^2, sodium salicylate layer. A very definite absorption hole appears at 2700Å and it is concluded that the decrease in yield at 2700Å observed here for thin layers is due to the fact that all the incident radiation is not absorbed. Yield measurements taken at 80°K, shown in Figure 5, seem to support this reasoning. The yield, although flat at room temperature, now shows a decrease at 2700Å brought about by a deepening of the absorption hole due to a sharpening of the absorption spectrum with decreasing temperature. The increase in the magnitude of the yield on cooling is~25% as expected from the results of emission spectrum

measurements. Also of interest in Figure 5 is the fact that the decrease between 2200 and 2000Å seems to be independent of temperature.

Figure 6 shows the relative quantum yield of sodium salicylate as measured with the vacuum apparatus of Figure 1a. Curve 6a shows data for six samples, all of thickness greater than 1.5 mg/cm^2, which did not show the drop in yield at 2700Å. Curve 6b is for thinner samples, $t < 1$ mg/cm^2, which did show the hole at 2700Å. A definite minimum is evident in both curves at 2000Å but here the drop is larger for thick samples, amounting to approximately 20% and the yield does not return to as large a value on the short wavelength side. For the thinner samples the drop is of the order of 10% and the yield values on either side are equal. Absorption data, as well as the behavior with thickness and temperature, see to rule out any explanation in terms of variation of absorption. The reason or reasons for this decrease at 2000Å, which we wish to emphasize has been observed in two independent series of measurements, will therefore be left as an unresolved question.

CONCLUSIONS

On the basis of our measurements it would appear that the appropriate thickness for sodium salicylate layers for use at room temperature should be between 1.5 and 6.5 mg/cm^2;

thicker layers show a slight decrease in efficiency due to increased reabsorption of the luminescence by the phosphor, while at lower temperatures somewhat thicker samples should be employed. Under these conditions the yield is essentially flat from 2200Å to near 3400Å.

ACKNOWLEDGEMENTS

We wish to thank Professor D. B. Dutton for his interest and suggestions regarding this work.

REFERENCES

1. G. Dejardin and R. Schwegler, Rev. Optique 13, 313 (1934)
2. F. S. Johnson, K. Watanabe and R. Tousey, J.O.S.A. 41, 702 (1951)
3. K. Watanabe and C. Y. Inn, J.O.S.A. 43, 32 (1953)
4. J. F. Hamann, Z. angw. Physik 10, 187 (1958)
5. N. Kristianpoller and D. B. Dutton, Appl. Optics, in press
6. A. M. Smith, Thesis, University of Rochester, 1961
7. J. E. Eby, K. J. Teegarden and D. B. Dutton, Phys. Rev. 116, 1099 (1959)

LIST OF ILLUSTRATIONS

Figure 1a — Schematic diagram of the arrangement for measuring excitation spectra in the non-vacuum UV. L = light source; C = 13 cycle chopper; B&L = Bausch and Lomb grating monochromator; NS = entrance slit; XS = exit slit; M = concave mirror (10 cm F.L.); S = phosphor sample, shown in "position A" (see text); PM = photomultiplier detector of the luminescence; T = radiation thermocouple.

Figure 1b — Schematic diagram of the arrangement for measuring excitation spectra in the vacuum UV. L = light source; M = vacuum monochromator; G = grating; C = 13 cycle chopper; S = phosphor sample; P = pyrex light pipe; PM = photomultiplier; T = radiation thermocouple.

Figure 2 — Emission spectra of sodium salicylate at room temperature (a) and at 80°K (b).

Figure 3 — Relative quantum yield of three sodium salicylate samples as measured with the apparatus illustrated in Figure 1a. Sample 1: $t \simeq 1.3$ mg/cm^2; sample 2: $t \simeq 1.6$ mg/cm^2; sample 3: $t \simeq 0.2$ mg/cm^2.

Figure 4 — Absorption spectrum of a thin ($t \simeq 0.2$ mg/cm^2) sodium salicylate sample.

Figure 5 — Relative quantum yield of one sodium salicylate sample at room temperature and at 80°K.

LIST OF ILLUSTRATIONS (cont'd.)

Figure 6 Relative quantum yield of sodium salicylate as measured using the apparatus illustrated in Figure 1b.

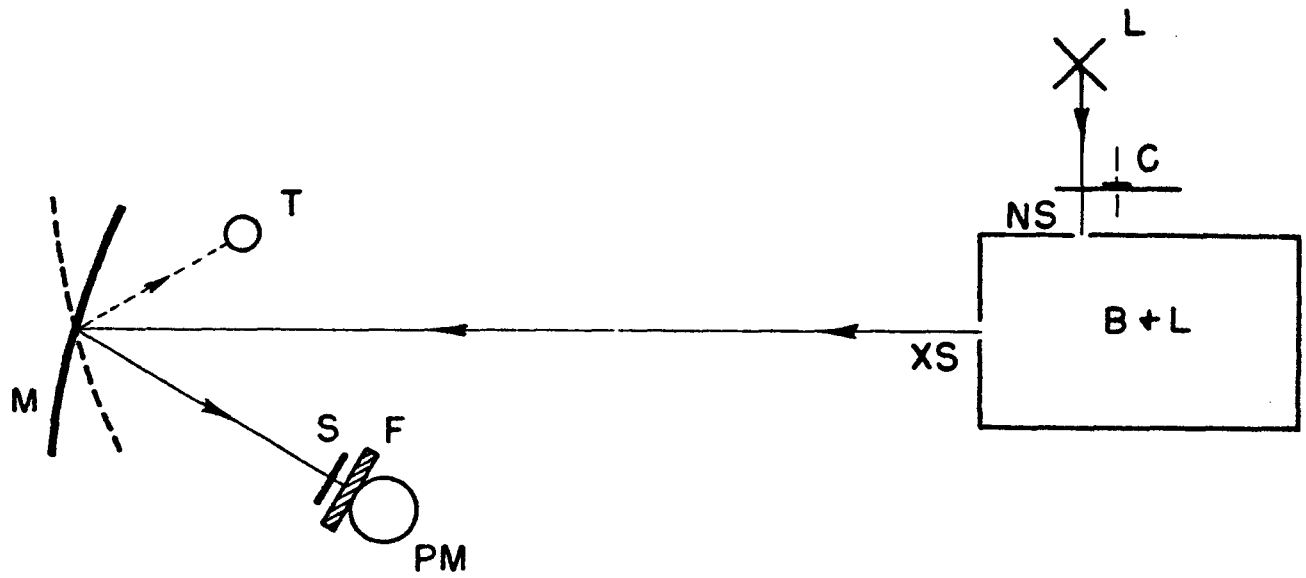


Figure 1a. Schematic diagram of the arrangement for measuring excitation spectra in the non-vacuum UV. L=light source; C=13 cycle chopper; B&L=Bausch and Lomb grating monochromator; NS= entrance slit; XS=exit slit;M=concave mirror (10 cm F.L.);S= phosphor sample, shown in "position A"(see text); PM=photo-multiplier detector of the luminescence;T=radiation thermocouple.

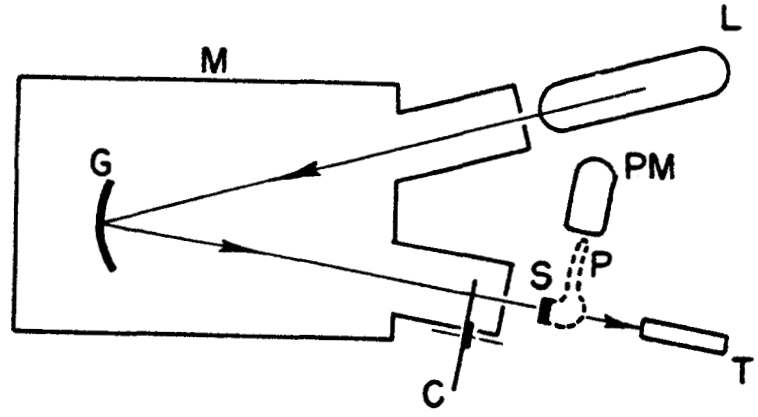


Figure 1b. Schematic diagram of the arrangement for measuring excitation spectra in the vacuum UV. L=light source; M=vacuum monochromator; G=grating; C=13 cycle chopper; S=phosphor sample; P=pyrex light pipe; PM=photomultiplier; T=radiation thermocouple.

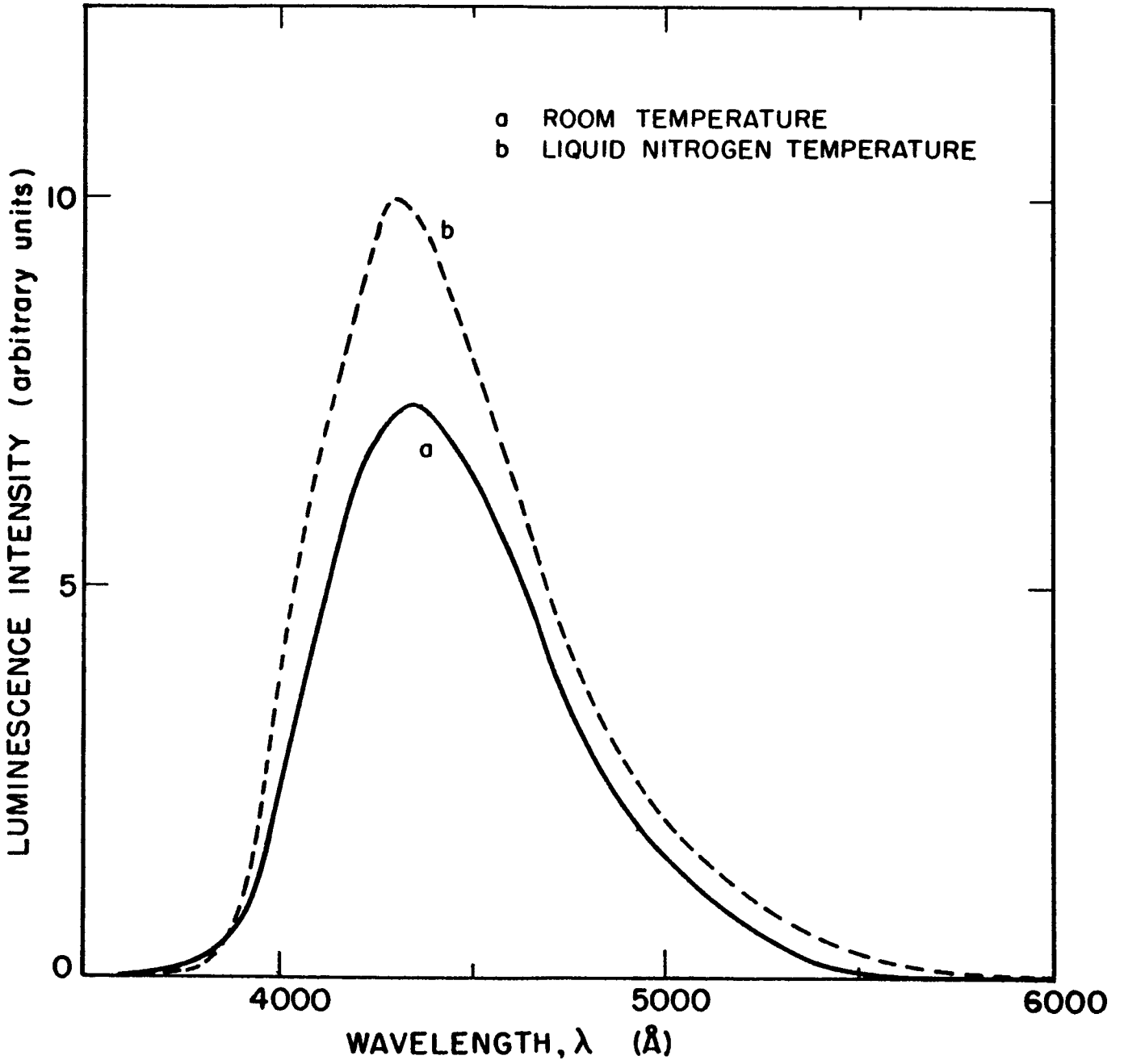


Figure 2. Emission spectra of sodium salicylate at room temperature (a) and at 80°K (b).

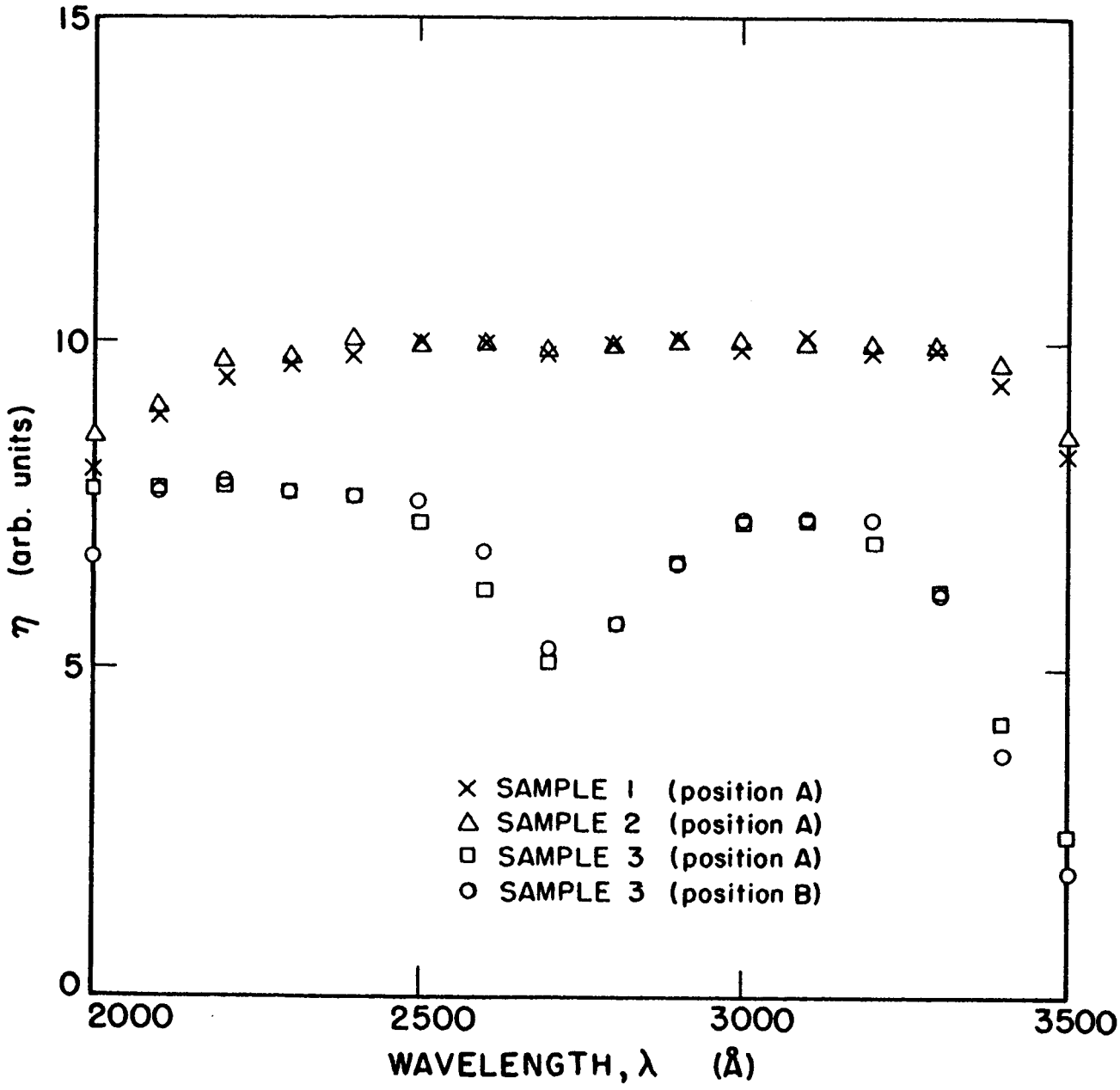


Figure 3. Relative quantum yield of three sodium salicylate samples as measured with the apparatus illustrated in Figure 1a. Sample 1: $t \simeq 1.3$ mg/cm^2, Sample 2: $t \simeq 1.6$ mg/cm^2, Sample 3: $t \simeq 0.2$ mg/cm^2.

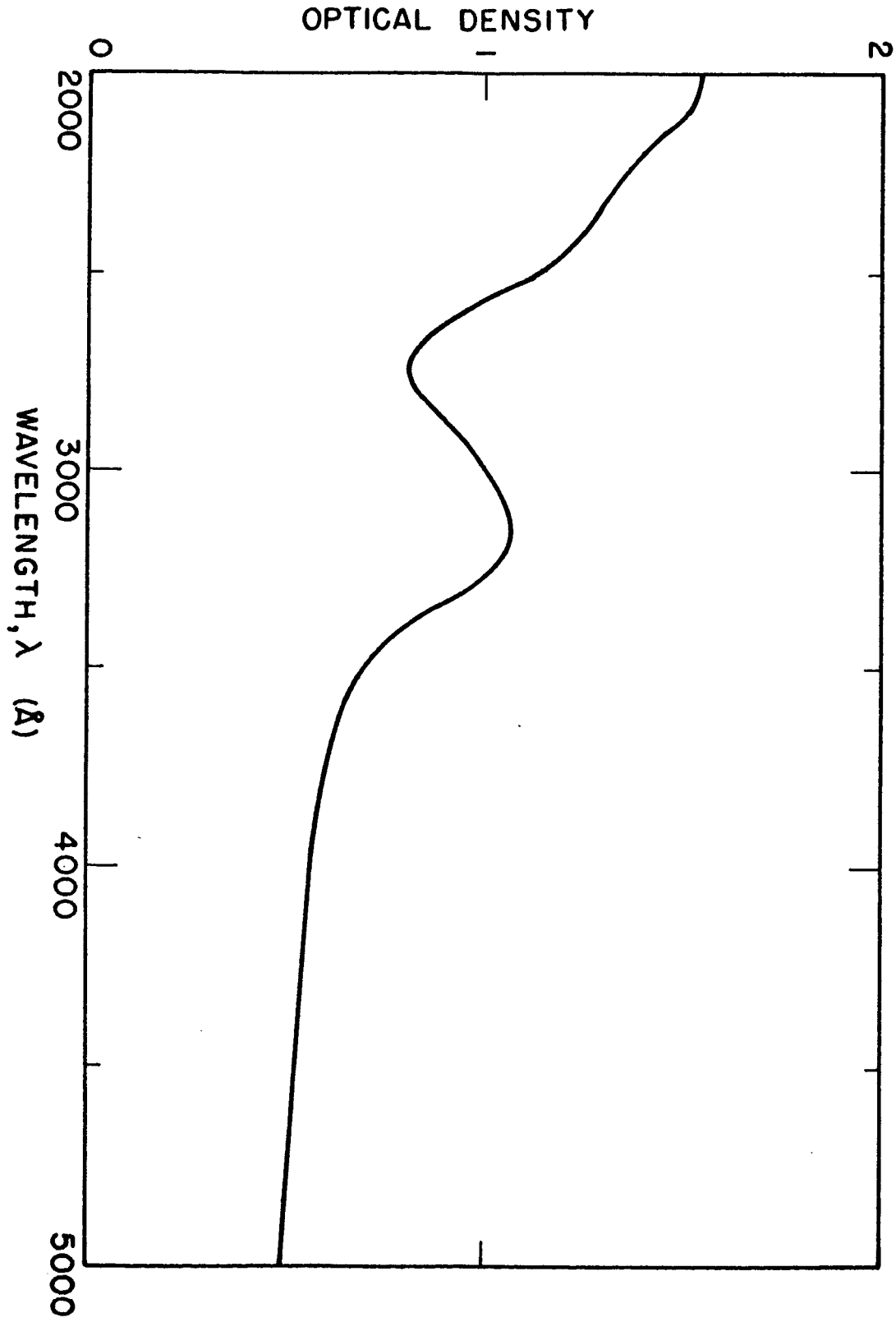


Figure 4. Absorption spectrum of a thin ($t \simeq 0.2$ mg/cm^2) sodium salicylate sample.

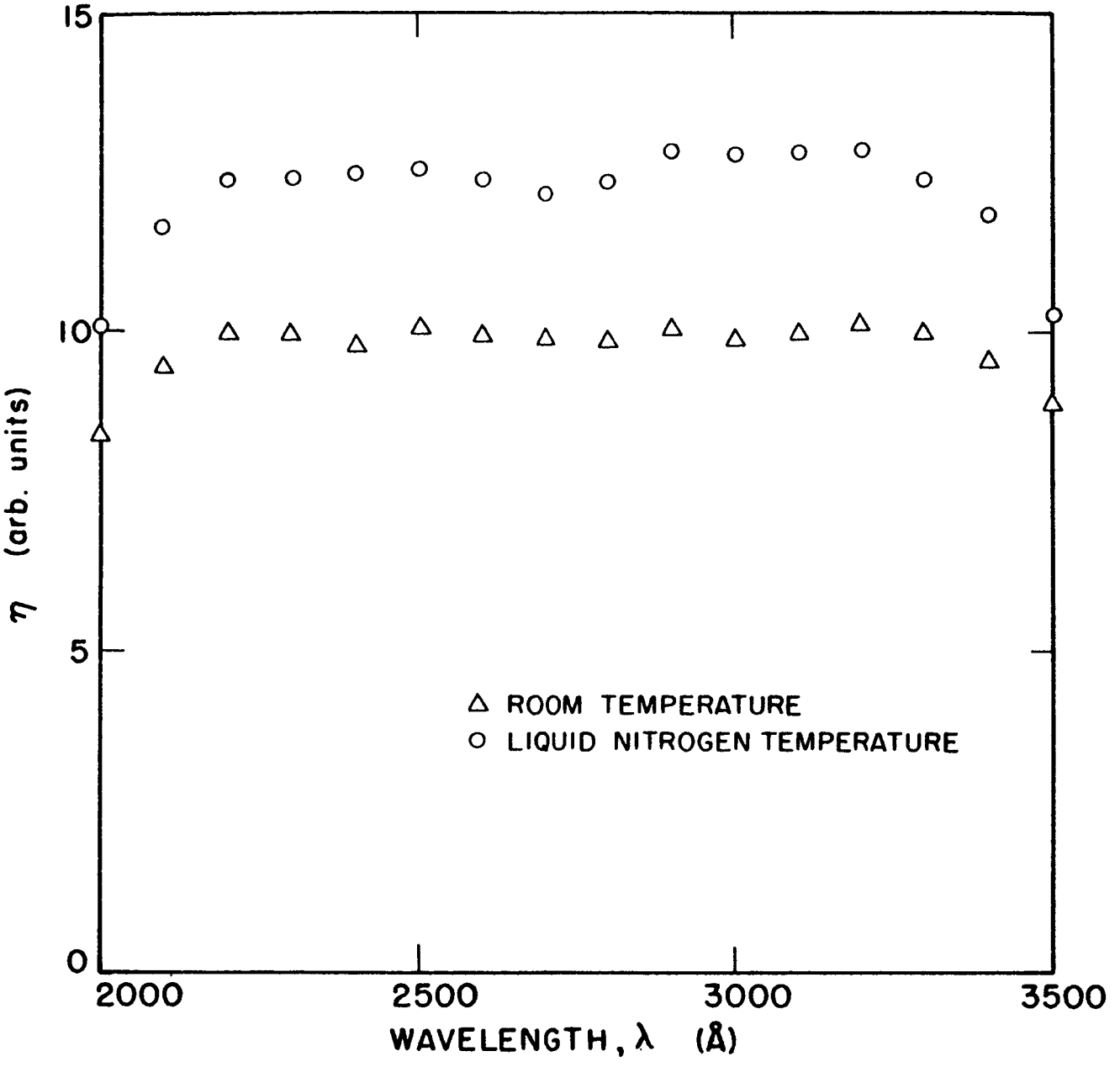


Figure 5. Relative quantum yield of one sodium salicylate sample at room temperature and at 80°K.

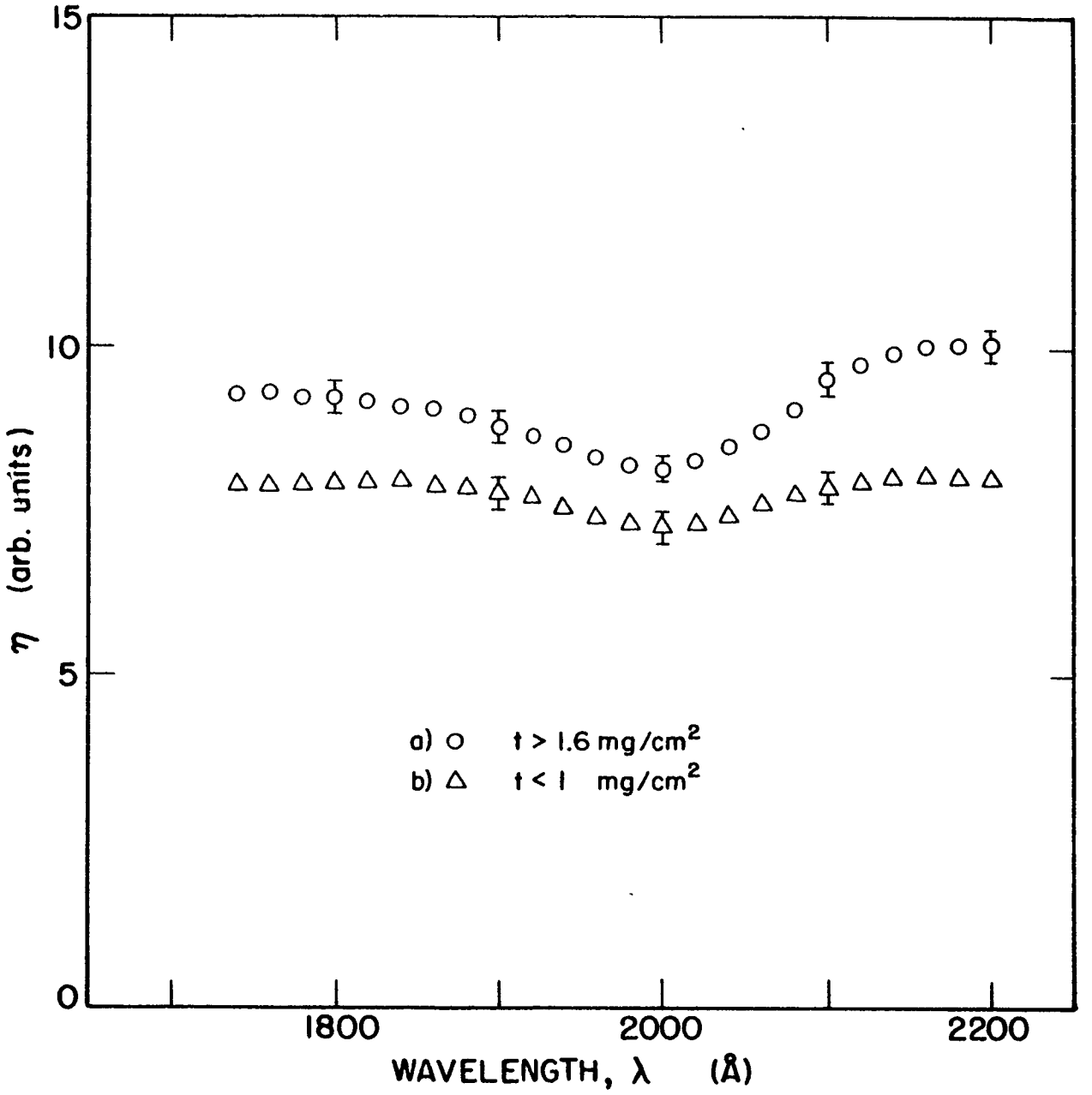


Figure 6. Relative quantum yield of sodium salicylate as measured using the apparatus illustrated in Figure 1b.

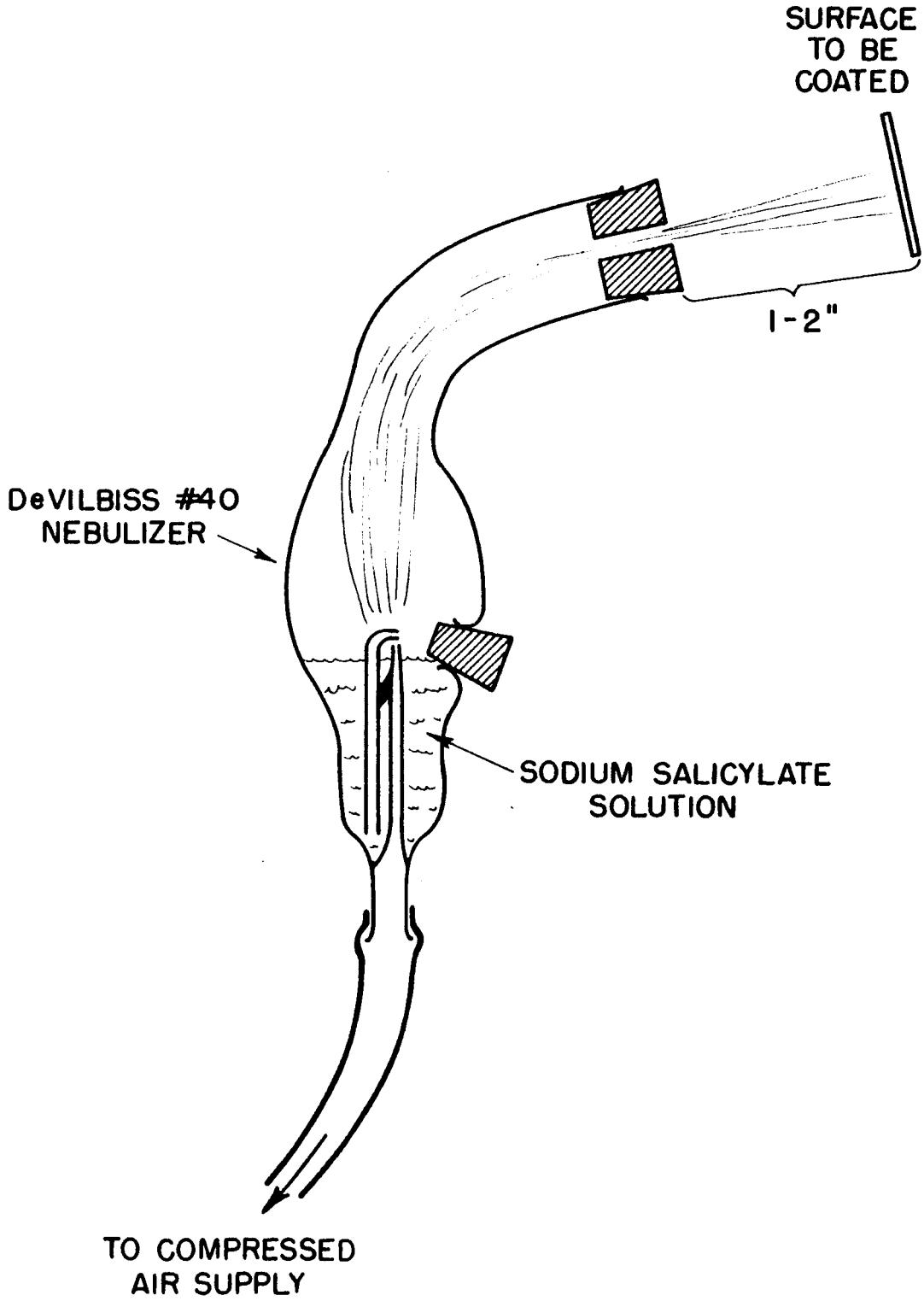
APPENDIX

A SIMPLE METHOD FOR PREPARING SODIUM SALICYLATE FILMS

Of the various methods developed for the preparation of sodium salicylate films, probably the most widely used is the spraying technique. Using a standard atomizer, however, the method is time consuming and the danger exists of the formation of voids in the film caused by large drops which may reach the surface being coated. The technique described here avoids these complications and in addition results in much more uniform and fine grained layers than can be easily made with a standard atomizer.

A commercially available nebulizer for aerosol therapy* is modified as shown in the figure by the addition of a small aperture at the output end. The nebulizer produces an extremely fine spray, i.e. small droplet size, which is directed through the aperture onto the surface to be coated. We have found that, depending on the speed desired, holes of 1/16 to 1/32" are adequate. The use of a low air pressure, 1 to 2 lb/sq. in. avoids the possibility that any large drops, which may be accidentally formed, will reach the sample being coated. Since the mist dries on contact the coating may be applied continuously and uniform layers of any desired thickness may be produced in minutes.

* DeVilbiss Glass Nebulizer #40, The DeVilbiss Company, Somerset, Pennsylvania, available in most drug stores.



Appendix Figure